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EFFECT OF COPPER COATING ON THE PHYSICAL AND ELECTROCHEMICAL PROPERTIES OF CONDUCTIVE PLA FILAMENT

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ABSTRACT

3D printing method known as additive manufacturing (AM), is a new technology that allows to design and production of objects or operational devices in a single process. 3D technology has expanded its ability to utilize as scientific research and medical application, recently. As long as this technology becomes more common, the 3D printing method will be easier to achieve. Especially, the 3D printing method has been used to perform electrodes production for electrochemical applications in the last five years. Commonly known 3D printing filaments are Polylactic Acid (PLA) or Acrylonitrile Butadiene Styrene (ABS). Thanks to these conductive materials, it is possible to modify their material properties to enhance conductivity or other specifications. In this study, investigation of the electrochemical performance of the conductive PLA is conducted by electroplating of copper (Cu) on the surface. In the constant voltage value, the current density value of Cu coated electrode specimen is increased three times. Moreover, the usability of conductive PLA as an electrical circuit element or electrochemical energy conversion electrode is investigated. According to the obtained results, in the Lineer Sweep Voltammetry (LSV) measurements, uncoated PLA and Cu coated PLA specimen has a maximum current of 0.9A and 2.8A at a constant voltage, respectively. In the Cyclic Voltammetry (CV) measurement, kinetic performance and electrical conductivity properties are improved in Cu coated PLA specimen. In the CV measurements, for different scan rate between 50 mV to 200mV is observed that the current value of Cu coated PLA specimen is increased for all measurements. In the Cu coated PLA specimen, significant improvement in conductivity is obtained in Electrochemical Impedance Spectroscopy Analysis (EIS).

Keywords: Conductive Filament. PLA. Electroplating. Cu Coating. 3D Printing. Material Science.

1. INTRODUCTION

The 3D printing method, also known as AM, is a new technology that allows the design and production of objects or operational devices in a single process. The 3D printing method which is used as a rapid prototyping tool for industrial applications is utilized in scientific and medical applications such as, microvascular systems, orthopedic implants, rehabilitation aid tools, electronic devices, electrochemical systems [1]. As this technology became widespread, prototyping by 3D printing systems became more accessible and increased their use in research laboratories [2]. According to the literature, 3D printing technology has been used to perform electrodes production for electrochemical applications in the last five years. In order to use the Selective Laser Melting (SLM) technique in the production of electrodes, 3D printing of the metal electrodes requires high-cost printers, and modification is required as an active catalyst for the practical application of the electrodes. However, a commonly known alternative selection is the 3D printing of PLA or ABS with a conductive material [3].

The PLA has played an essential role in the investigation of polymer materials due to its biodegradability and good mechanical properties. In addition, cost-effective electrical elements or electrodes are very important for the sustainability of the future energy conversion [4]. However, there are also disadvantages such as that the PLA is fragile, low impact resistance and high cost in commercial applications. Therefore, the physical and/or chemical modification of PLA is required. The composition of conductive fillers such as graphene, carbon black, graphite and biodegradable polylactic acid can be used together to improve the performance of polylactic acid [5]. The ABS is an important polymer material which is commonly utilized in the industry because of its mechanical properties, high chemical resistance, and easy process. Different applications of ABS are used primarily in building and construction, personal care products, toys, computer equipment, medical devices, chemical systems, and automotive components [6]. One of the major disadvantages of ABS is its natural flammability and therefore it is necessary to increase its thermal stability and flame-retardant properties [7-9]. The 3D printing of the conductive polymer materials can be used less cost than the 3D printing of the metallic materials as the Fused Deposition Modeling (FDM) technique. [10]. Black Magic conductive PLA filament is commercially available and it becomes more popular in laboratories as it can be used in low-cost FDM 3D printers for the production of electrodes. [11, 12]. Although there are important investigations about conductive materials, these materials are inaccessible, easily. At present, carbon black and graphene-based electrically conductive plastic composite filaments are available for 3D printers as Fused Filament Fabrication (FFF). To obtain a higher rate connection among the electrical or mechanical design parts of 3D printed materials, there is a need to characterize, design and create the conductive materials [13]. Moreover, the production methods of 3D printing techniques such as Stereolithography (SLA) and FDM have been studied in an integration to the 3D electronics studies. Though the production technology allows for complete production of high-quality prototypes, there are still significant challenges in the production stage. In order to overcome these challenges in the future of 3D printing electronics, new generation circuit devices are being developed [14]. In addition to polymers and conductors, several materials can be used to create different functional electronic devices such as 3D printed microelectronics, semiconductor, magnetic and piezoelectric materials [15]. Recently, using dielectric ceramics, decomposition polymers and the composites of these materials have focused on the production of capacitors having high energy density. Although there has been essential progress in the development of such materials, it has been limited to the manufacturing process and available technology, especially for complex structures [16]. Usually, metal composite materials can be produced using a various application such as hot pressing, casting, thermal spraying, cold spraying, and electrochemical deposition. Among these techniques, electrodeposition method has attracted great interest in the literature due to its low cost, and facility to operate under normal conditions and under normal pressure [17]. Electrochemical deposition is an effective method in the preparation of multifunctional composite coatings (such as ZnO, Al_2O_3, Cu-Al [18-20]) and their design requirements, both physical and chemical performances of composite materials can be controlled by electrochemical coating [21].

In this study, the electrochemical performance of the conductive PLA filament is investigated using the Cu electroplating technique. The physical and electrochemical properties are measured by Scanning Electron Microscope (SEM), SEM- Energy-Dispersive X-ray spectroscopy (EDX), CV, LSV and EIS techniques.

2. MATERIAL AND METHOD

The PLA filament purchased from Prota-Pasta commercially is cut 8 cm long without printing on 3D printer and electrochemical coating process is performed in 0.5M H_2SO_4 solution using Cu electrodes in constant current in 0.01A. Electrode distance is fixed as 10 mm between Cu and PLA samples. Electrical power is supplied by electrical power supply, voltage and current values are measured by voltmeter. Figure 1 shows the electroplating procedure view of the PLA and Cu electrodes. In order to use the same active surface area, the regions without coating have wrapped with Teflon tape. 57.38 mm^2 is selected as surface area of uncoated and Cu coated surface area. The CV and LSV measurements of both uncoated PLA and Cu coated PLA specimen are conducted using these electrode samples.

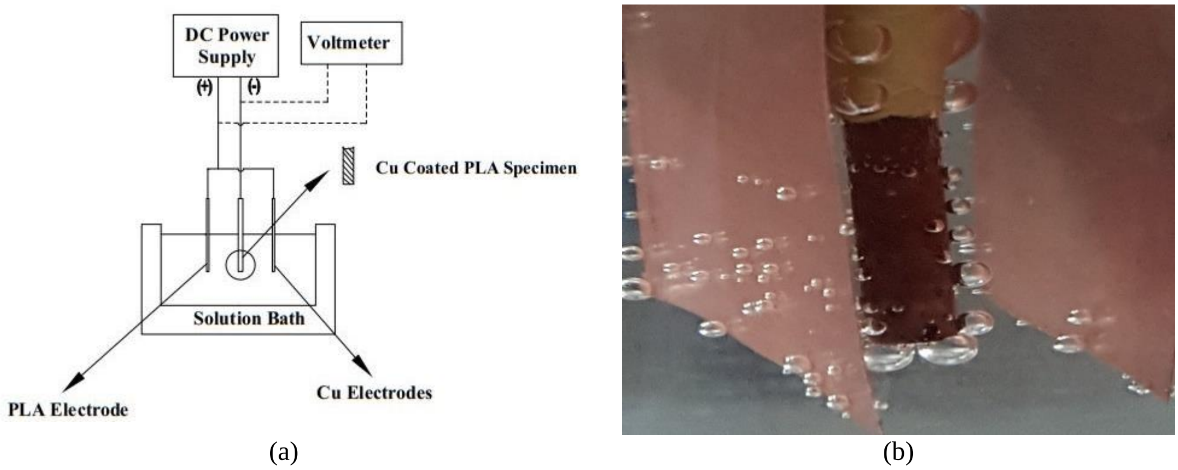


Figure 1. a) Electroplating procedure view of the PLA and Cu electrodes. b) Cu coating process in 0.5M H_2SO_4 solution.

Figure 2 shows the three-electrode electrochemical cell configuration for CV and LSV measurements. The electrochemical characterization techniques are performed using potentiostat (VersaStudio/ Versastat) by three-electrode technique CV and LSV measurements are analyzed in 0.5 M H_2SO_4 solution using Pt as the counter electrode, 1M KCl saturated Ag/AgCl is used as a reference electrode and Cu coated PLA specimen is used as a working electrode in three electrode electrochemical cell configuration. CV measurements are investigated with scan rates 50, 100, 200 mV/s and LSV measurements are conducted in 10 mV/s scan rate. Surface morphology of Cu coated PLA specimen is measured using SEM and SEM-EDX.

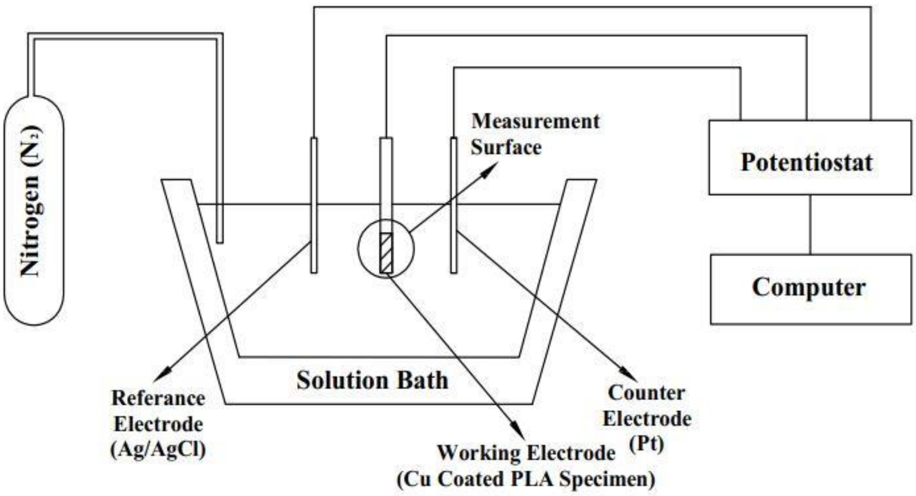


Figure 2. Three-electrode electrochemical cell configuration.

In Figure 3, it can be seen uncoated and Cu coated PLA specimen electrodes. In the active surface region, coating of Cu material can be seen in orange colour. The other surfaces are insulated by Teflon tape during electrochemical measurements.

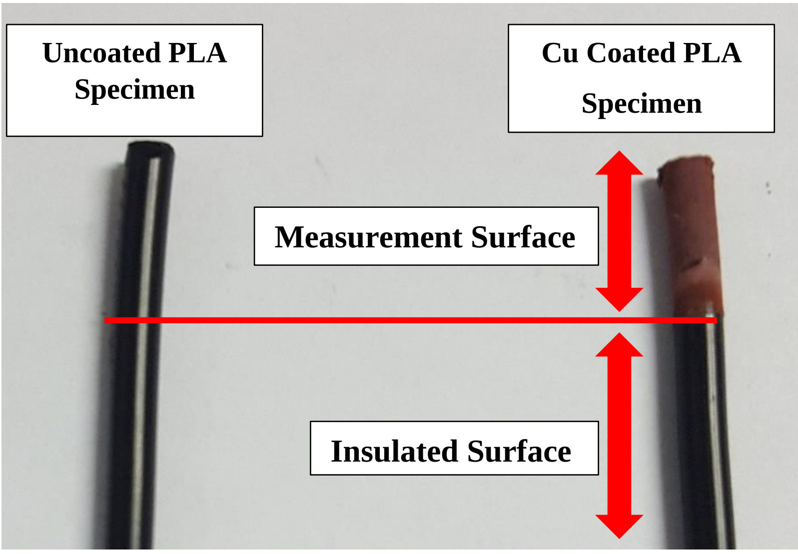


Figure 3. Uncoated and Cu coated PLA specimens.

3. EXPERIMENTAL RESULTS

In Figure 4, SEM image of the Cu coated PLA specimen electrode can be seen. It can be observed that the thickness of the coating is about 1.123 microns and the homogeneous accumulation of Cu is obtained during the experiments.

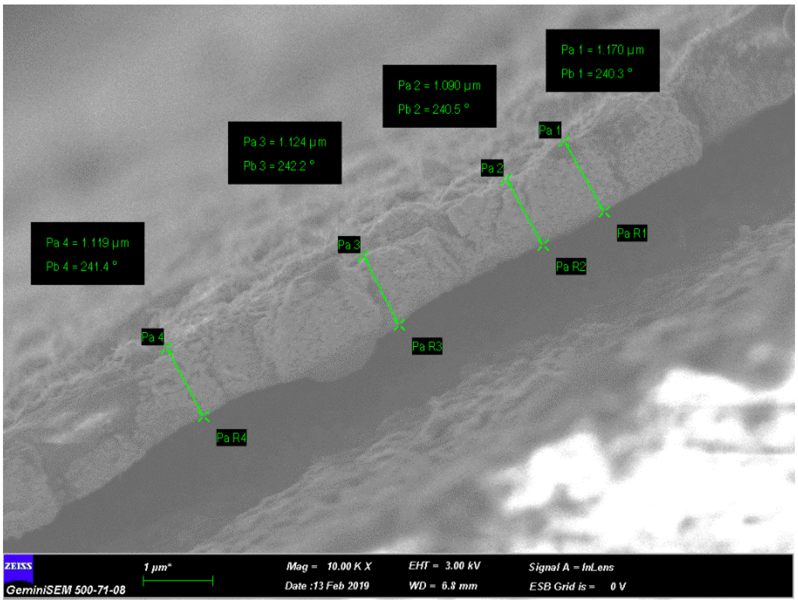
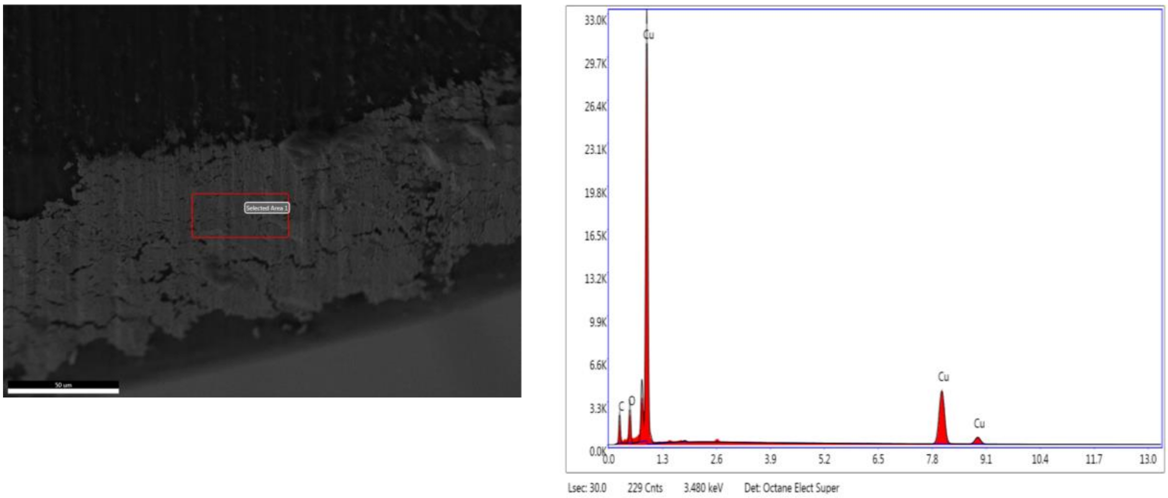


Figure 4. SEM image of the Cu coated PLA specimen electrode.

Thickness in Figure 4 also shows the homogeneous coating of Cu on the surface of PLA specimen. The SEM-EDX image and EDX spectrum of Cu coated PLA specimen electrode are shown in Figure 5 and weight and atomic rate of elements can be seen in Table 1. According to the measurements taken from the red selected area, weight ratio of Cu is obtained around 65 %.



(a) (b)

Figure 5. SEM-EDX image of Cu coated PLA specimen a) selected region, b) SEM-EDX spectrum

Table 1. Weight an atomic rate of elements.

Element	Weight %	Atomic %	Net Int.
C	22.54	50.63	355.63
O	13.08	22.05	571.16
Cu	64.38	27.33	2176.04

Other weight ratios such as C and O are due to the polymer structure of PLA. Carbon is obtained around 22.54% and Oxygen weight ratio obtained 13.08%. CV measurements of uncoated PLA and Cu coated PLA specimens ranging from 50 mV to 200 mV are given in Figure 6, 7 and 8 respectively.

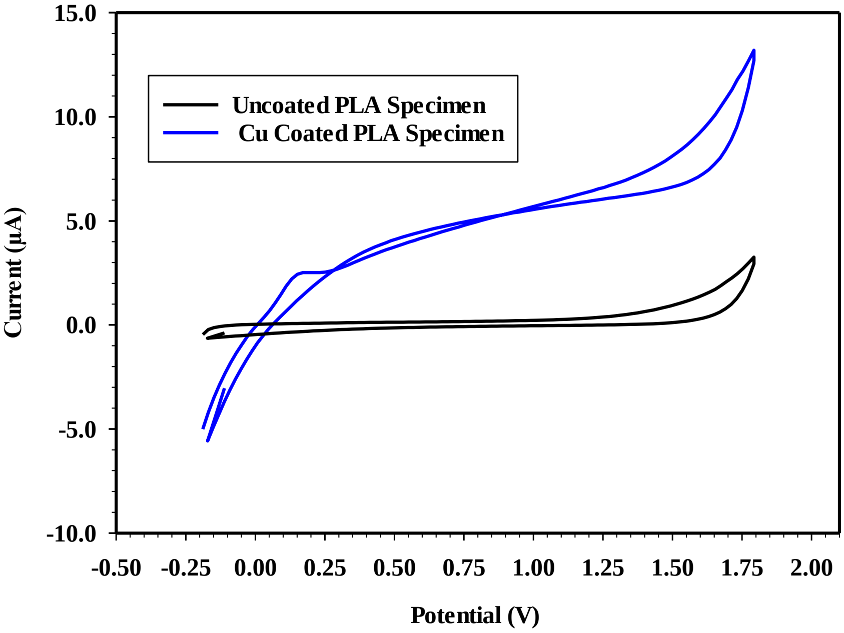


Figure 6. CV measurements of Cu coated and uncoated PLA specimens in the 50 mV.

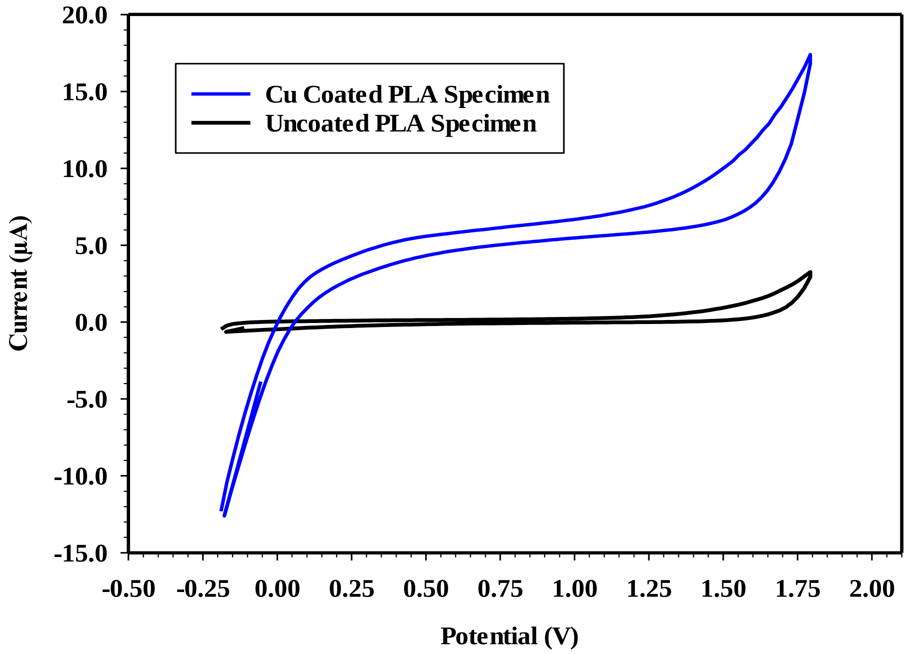


Figure 7. CV measurements of Cu coated and uncoated PLA specimens in the 100 mV.

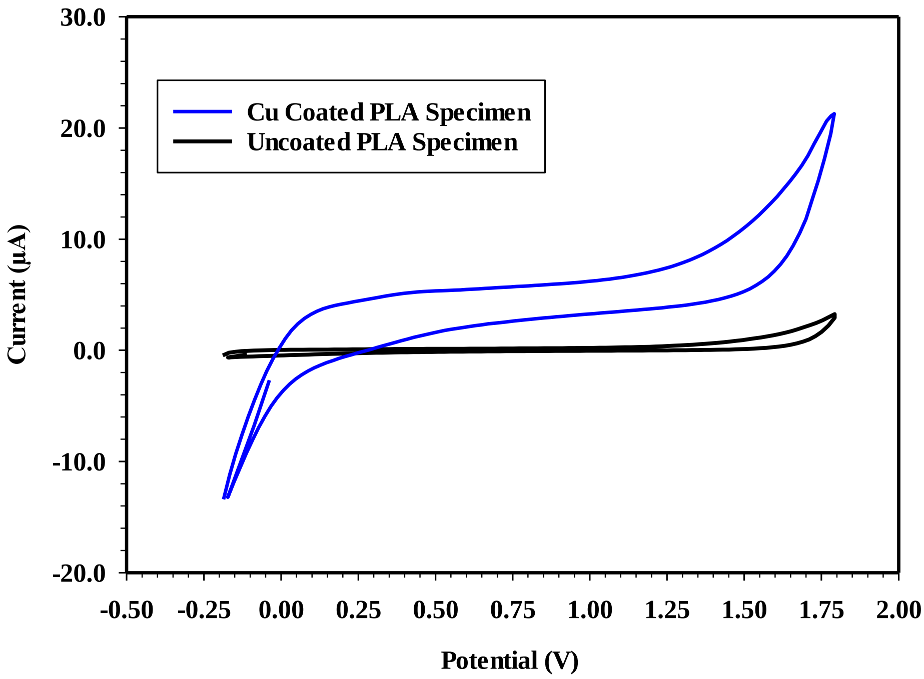


Figure 8. CV measurements of Cu coated and uncoated PLA specimens in the 200 mV.

As can be seen from the CV measurements, Cu coated PLA specimen shows three times higher current in the constant voltage. This increment is higher in the hydrogen production region during the adsorption reactions. Improvement of current value is more dominant in 50mV scan rate. The current values of Cu coated PLA specimen at 50 mV, 100 mV, and 200 mV scanning rate are 13 µA, 17 µA, and 21 µA, respectively. These results show that, coating of PLA specimen with conductive media improves its kinetic activity. Moreover, it is possible to obtain efficient hydrogen production electrodes with this method. In Figure 9, LSV measurement of Cu coated and uncoated PLA specimens can be seen.

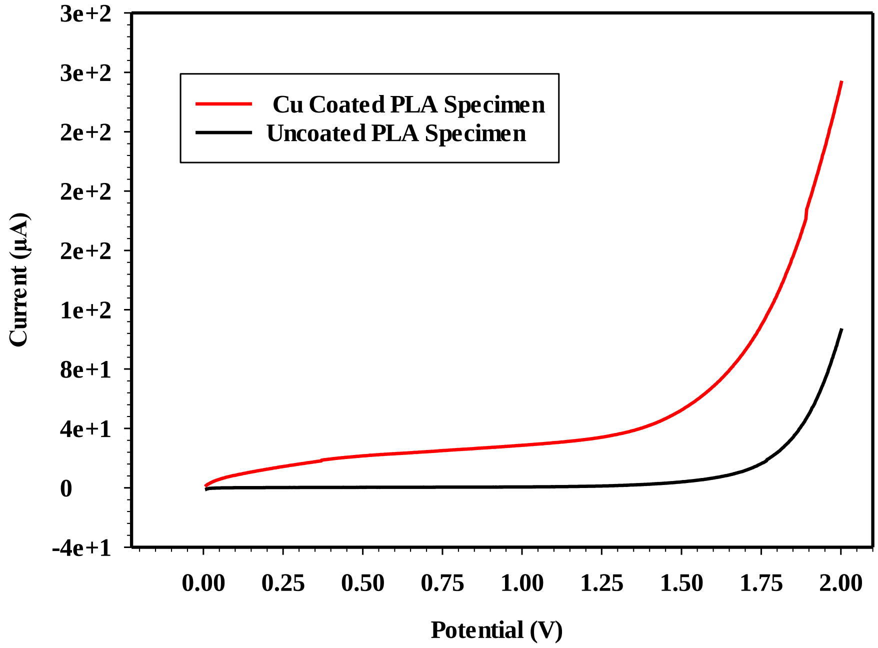


Figure 9. LSV measurements of Cu coated and uncoated PLA specimens.

As shown in Figure 9, in the LSV curve, 2.7 times more current is observed in the 2V constant voltages thanks to the Cu coated PLA specimen. It can be concluded that the ohmic and mass transfer losses have been reduced and the conductivity of the PLA has been increased. These results show the usability of 3D printing technologies using conductive PLA in electrical and the electrochemical applications by increasing the conductivity with Cu coating. In Figure 10, EIS measurement of Cu coated and uncoated PLA specimens can be seen.

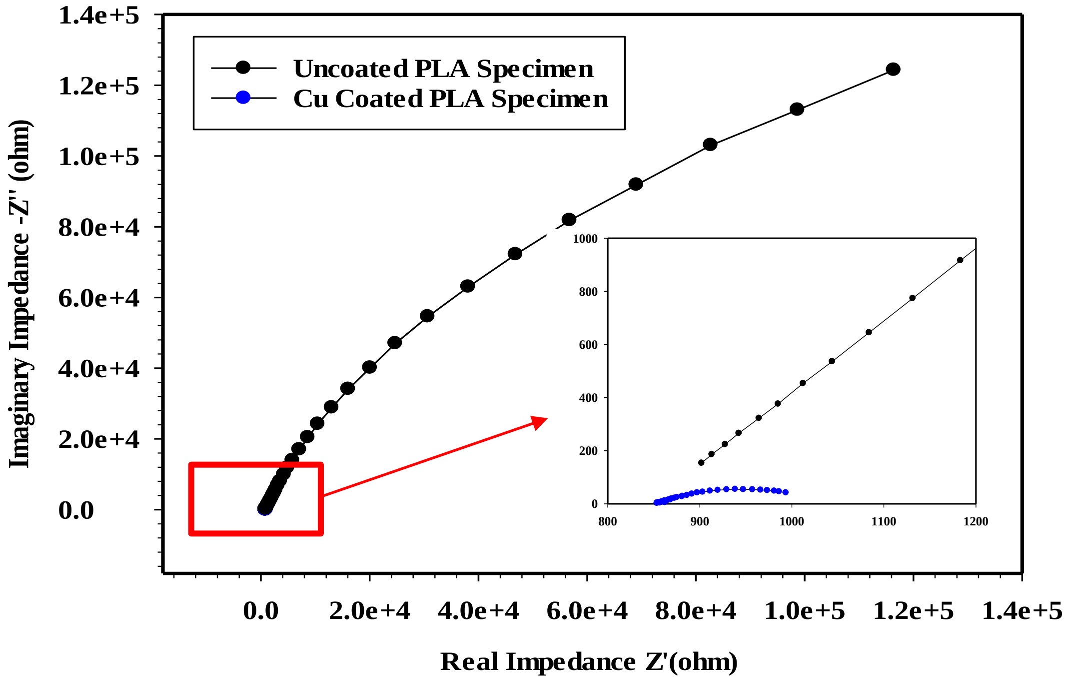


Figure 10. EIS measurements of Cu coated and uncoated PLA specimens.

During the EIS measurement, 10kHz frequency is used for both electrodes versus open circuit potential. As shown in Figure 10, it is seen that the highest resistance obtained in uncoated PLA specimen. When PLA filament is coated with Cu, it is seen that the resistance is reduced, significantly.

4. CONCLUSION

As can be seen from the results, the conductivity of the PLA material has increased, significantly. Cu metal has been successfully electroplated with a thickness of 1.123 microns. Although it is a thin coating, the current value of PLA based electrode in 2V is increased around three times compared to the uncoated PLA. According to the results obtained from the LSV measurements, it is seen that the uncoated and Cu coated PLA specimens have maximum current of 0.9A and 2.8A at a constant voltage, respectively. In the CV measurement, after Cu coating, kinetic performance of PLA material is increased, and its electrical properties are improved. As a result, thanks to development of 3D printing technologies, ability to use different shaped geometries will be possible to design unique electrical circuits, electrodes, capacitors, sensors or other related accessories.

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